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Thermal extremes can intensify chemical toxicity to freshwater organisms and hence exacerbate their impact to the biological community

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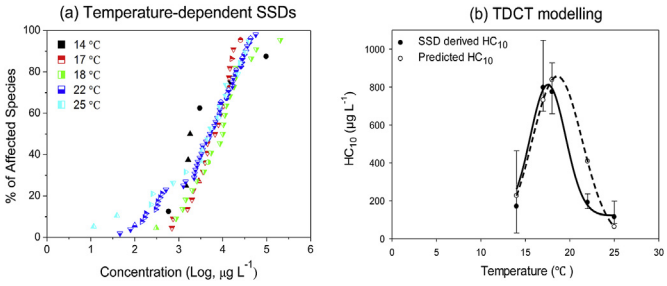
HIGHLIGHTS

- Freshwater species mainly follow negative linear and inverted-V shaped TDCT models.
- The inverted-V shaped model can better describe temperature–toxicity relationship.
- The inverted-V shaped relationship was characterised by temperature-dependent HC_{10}s.
- A mathematical model was developed to validate the inverted-V shaped model.

GRAPHICAL ABSTRACT



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ABSTRACT

Temperature in freshwater ecosystems fluctuates daily, seasonally and yearly. Climate change further induces temperature variations. In this study, we hypothesise that water temperatures, in particular thermal extremes, can significantly influence chemical toxicity to ectothermic organisms. Although temperature-dependent chemical toxicity (TDCT) is a classic research area in ecotoxicology, a unified model for predicting TDCT for freshwater species is yet to be developed. This study aimed to address this challenging issue through a meta-analysis by comparing acute toxicity endpoints (i.e. median lethal or effective concentration data; LC_{50} or EC_{50}) of 13 chemicals for various freshwater species generated from different temperatures. Our results suggest that in most cases, freshwater species exhibit the highest tolerance towards chemicals at their physical optimal temperature (T_{opt}), and chemical toxicity exacerbates when temperature is higher or lower than T_{opt} (i.e. inverted V-shaped model between temperature and LC_{50} or EC_{50}). Such observations are further supported by temperature-dependent hazardous concentration 10% (HC_{10}) values derived from species sensitivity distributions constructed using toxicity data generated at different temperatures. A unified mathematical model was also developed to describe the inverted V-shape relationship between temperature and HC_{10} derivations. Overall, considering the

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natural variations of freshwater temperatures, the inverted V-shaped TDCT model can be readily applied to derive water quality guidelines and assess ecological risks of chemical contaminants.

1. Introduction

Water temperatures fluctuate daily, seasonally and yearly in freshwater ecosystems. Physicochemical properties, bioavailability and toxicity of a chemical can be influenced by temperature change (Cairns et al., 1978). Furthermore, anthropogenically driven climate change not only results in increasing ambient and water temperatures but also leads to more frequent and long-lasting cold and heat waves (US Department of the Interior, 2009; IPCC et al., 2014). As postulated, global warming results in climatic change, which is more unpredictable with increasing extreme weather events (Barnett et al., 2005), including larger temperature fluctuations and more frequent extreme temperature events occurring in the future (IPCC et al., 2014). Temperature variations and thermal extremes caused by climatic change are expected to have profound implications on chemical toxicity to individual aquatic organisms, which will in turn influence the size and structure of their population, the species composition of communities and the structure and functioning of the ecosystem (Pörtner and Knust, 2007).

Before predicting how climatic change interacts with the impact of chemical pollution on freshwater ecosystems, it is essential to ascertain the relationship between thermal stress and chemical toxicity to freshwater organisms. It is commonly reported that chemical toxicity increases with increasing temperature (e.g. Cairns et al., 1978; Leung et al., 2000; Kwok and Leung, 2005), following a negative relationship (Model-I; Figs. S1a–c) between temperature and toxicity endpoints such as median lethal or effective concentration (LC_{50} or EC_{50}). Such a negative linear response can be typically explained by the temperature-regulated mechanisms. For instance, high temperature would increase water solubility of toxicants, elevate their reactivity rate and bioavailability and hence increase their toxicity as reflected by having low LC_{50} or EC_{50} values (Heugens et al., 2003). This linear response was also partly attributed to the decreasing solubility of oxygen in aquatic organisms under high temperature environments (Cairns et al., 1978). Alternatively, some ectotherms could enter dormancy (i.e. metabolic depression) at low temperatures, leading to a reduced uptake of the chemical and hence lowering the chemical toxicity (Bao et al., 2008).

However, it should be noted that in some cases, such a simple linear function between temperature and chemical toxicity could not account for species' performances under a wide range of temperatures with extreme thermal conditions (Angilletta, 2006). Pioneer studies of the temperature-dependent chemical toxicity (TDCT) conducted on a wide range of aquatic organisms and chemicals have demonstrated chemical toxicity and temperature varying from no relationship to negative or positive relationships (Cairns et al., 1978). As demonstrated in more recent comprehensive toxicity studies, the relationship between temperature and chemical toxicity for some aquatic organisms follows a non-linear function (Bao et al., 2008; Lau et al., 2014; Zhou et al., 2014). For example, chemical toxicity is found to follow a cumulative U-shaped relationship (e.g. cumulative mortality with temperature) and is lowest at an optimal temperature (T_{opt}; Fig. S1d) (Sangita et al., 2012). For the majority of aquatic organisms, there was also an increasing recognition that many performances (e.g. feeding rate, growth and reproduction) are temperature dependent, thereby exhibiting a unimodal and asymmetric thermal performance curve (Fig. S1e) (Amarasekare and Savage, 2012). According to the thermal performance curve concept, an inverted V-shaped TDCT model (Model-II; Fig. S1f) has been proposed to describe the relationship between temperature and chemical toxicity to aquatic ectothermic organisms (Lau et al., 2014; Zhou et al., 2014). Both this Model-II and the aforementioned Model-I are, however, yet to be verified through a systematic examination of more freshwater species and more chemicals.

As individual species are integral components of the biological community in any freshwater ecosystem, their individual responses to temperature changes are likely to have significant effects at both population and community levels. This, therefore, raises the expected question whether Model II or Model I (founded on acute toxicity endpoints) can be extrapolated and applied to the effect thresholds at the community level. The effect threshold (e.g. hazardous concentration p%; HC_p) can be statistically derived from a species sensitivity distribution (SSD), that is, a cumulative distribution of toxicity endpoints of various species to the same chemical (Wheeler et al., 2002; Leung et al., 2005). However, the effect of temperature on SSDs has yet to be considered rigorously despite the SSD concept being widely used for establishing water quality guidelines (WQGs) (Stephan et al., 1985; OECD, 1995; ANZECC and ARMCANZ, 2000) and conducting ecological risk assessments (Solomon et al., 1996; van Straalen and van Rijn, 1998; Solomon et al., 2001). Consequently, the trigger value (e.g. hazardous concentration 10%; HC_{10}) derived from an SSD is treated as a temperature invariant, leading to a risk that the current WQG derived at a fixed temperature may not offer adequate protection to freshwater organisms from chemical exposure under different thermal conditions including extreme temperature events. Built upon the inverted V-shaped TDCT concept, we hypothesise that a temperature-dependent SSD model exists, where the temperature T_{opt} at which toxicity of a chemical is lowest with the largest HC_{10}, and toxicity increases when the temperature is above or below T_{opt} (similar to the Model-II).

This study was based on meta-analyses using secondary data and designed with three main objectives. First, it aimed to investigate the relationship between temperature and acute toxicity endpoints for a number of chemicals on an array of freshwater organisms under different temperatures to verify whether either of the two TDCT models (Model I or Model II) fitted well to the observed patterns. Second, it aimed to address the issue of temperature dependence in SSDs and its influence on the determination of HC_{10} values for protecting freshwater biological community. Third, a mathematical model was developed to describe the relationship between temperature and HC_{10} and to facilitate an estimation of HC_p at any temperature.

2. Methods

2.1. Data mining

Acute toxicity data (LC_{50}s and EC_{50}s) and corresponding experimental temperatures of freshwater species were extracted from the ECOTOX database of the United States' Environmental Protection Agency (http://www.epa.gov/ecotox/) and peer-reviewed

literature. Sources for the literature search included Web of Science, Scopus and Google Scholar, and only studies examining temperature effects to the same species and having more than two temperature points with the same exposure period were considered. Data were collected for 13 chemicals including six metals (arsenic, copper, lead, manganese, mercury and silver), five pesticides (carbaryl, chlordane, chlorpyrifos, lindane and malathion) and two narcotics (pentachlorophenol and phenol). To assure data quality, all original sources of the data were vetted, and only data generated from moderately reliable studies including tests based on nominal concentrations and tests without reporting the control mortality were used for the analysis (Wheeler et al., 2002). A geometric mean was used when there were multiple data of the same chemical for a species at each temperature point.

A comprehensive meta-analysis of various acute toxicity endpoints (i.e., LC_{50}s and EC_{50}s) for the 13 chemicals at multiple temperatures (i.e. $n \geq 3$) was conducted for acute toxicity data results from multiple studies (i.e. toxicity data of the same species collected from different studies conducted at different temperatures) and individual study (i.e. toxicity data of the same species collected from an individual study conducted at different temperatures), respectively. A linear regression was applied to statistically fit linear relationships (Model-I) between temperature and acute toxicity endpoints (SigmaPlot: version 12.0, San Jose, CA, USA). When the relationship followed the inverted V-shaped pattern (Model-II), a Gaussian function was used to fit the relationship (Deutsch et al., 2008). Fisher's exact test was also conducted to test the null hypothesis that the distribution of TDCT models was independent on study sources (i.e. multiple studies or individual study; significance level $\alpha = 0.05$; Microsoft Excel, 2016, Richmond, WA, USA).

2.2. Temperature-dependent SSDs

For each dataset of toxicity endpoints used for constructing an SSD at a given temperature, outlier(s) detected by Grubb's test or Tietjen-Moore test were excluded. Only datasets with a minimum of 7 data points from at least 3 different taxonomic groups were considered suitable for construction of SSDs, and a chemical with a minimum of 4 temperature-dependent SSDs was considered for subsequent TDCT modelling. Accordingly, only 7 chemicals fulfilled these requirements, including carbaryl, chlorpyrifos, copper, malathion, mercury, pentachlorophenol and phenol. To investigate the effect of temperature on a particular taxonomic group, a taxon-specific SSD was also constructed when more than 7 data points of species from the same taxon were available in a temperature-based dataset. Consequently, fish- and insect-specific temperature-dependent SSDs were generated for pentachlorophenol and chlorpyrifos, respectively.

The temperature-dependent SSDs were then constructed by following the procedures described in Wang et al. (2014). Briefly, toxicity data were ranked in ascending order and then fitted with 3 commonly used parametric models, namely, log-normal, log-logistic and Burr Type III regression models. The HC_{10} and its 95% confidence interval (95% CI) for each SSD were subsequently determined by the best-fit model approach (both Shapiro–Francia and Anderson–Darling (AD) tests passed with a minimum corrected Akaike information criterion (Min-*AICc*) value) (Wang et al., 2014). For each chemical, temperature-dependent SSDs for different temperatures were compared by a combination of analysis of covariance (ANCOVA; SPSS version 20, Chicago, IL, USA) and visual inspection (Leung et al., 2001; Wang et al., 2014). Relative species sensitivities at different temperatures for a chemical were also compared depending on calculated HC_{10} values and their 95% CIs using parametric one-way analysis of variance (ANOVA) and Tukey's post-hoc test or non-parametric Kruskal–Wallis test and Dunn's post-hoc test whenever appropriate (significance level $\alpha = 0.05$; GraphPad Prism™: version 5.00, San Diego, CA).

2.3. Effect of temperature on HC_{10}s

To predict physiological consequences of temperature on freshwater communities, we estimated a TDCT pattern for each chemical based on the relationship between temperatures and temperature-dependent HC_{10} derivations. For the observed non-linear relationships, Gaussian function was used to describe the increase in HC_{10} up to the T_{opt}, and the subsequent quadratic decline to the lowest value at the lowest and highest temperatures (Deutsch et al., 2008). For the observed linear relationships, a simple linear regression ($y = bx + a$) was employed to fit the data (SigmaPlot, version 12.0, San Jose, CA).

2.4. Mathematical model for deriving temperature-dependent HC_p

Currently, no rigorous formulation has been derived for describing the temperature effect on SSDs and hence the determination of the trigger values (i.e. HC_ps). In this study, an attempt was made to develop a suitable and reliable model to describe temperature-dependent SSDs and estimate HC_p at any given temperature. A mathematical framework was developed based on temperature-dependent SSDs, which were fitted with the log-normal model and the inverted V-shape relationship (i.e. Model II) between temperature and HC_p.

Considering a temperature-dependent SSD model, we define the random variable $x(p,t)$:

$$x(p,t) = f(p, \theta_1(t), \theta_2(t), \ldots, \theta_m(t)) \quad (1)$$

which denotes the HC_p at temperature t, where $\theta_1(t), \theta_2(t), \ldots, \theta_m(t)$ are the values of model parameters at temperature t.

For example, it is supposed that the concentration at temperature t is $M(t) \sim$ log-normal $(\mu(t), \sigma^2(t))$, where the model parameters $\mu(t)$ and $\sigma(t)$ change with t. Then, HC_p at temperature t and the temperature T_{opt} at which $x(p, t)$ attains its maximum are given by Equations (2) and (3), respectively.

$$x(p,t) = A(p)\tilde{x}(p,t) \quad (2)$$

$$T_{opt} = \frac{b_2 - b_1^2 c_1 c_2 \Phi^{-1}(p)}{1 - b_1^2 c_2 \Phi^{-1}(p)} \quad (3)$$

where, $A(p) = \exp[b_3 + c_3\Phi^{-1}(p)]$, $\tilde{x}(p, t) = \exp\left[-\left(\frac{t-b_2}{b_1}\right)^2 + c_2\Phi^{-1}(p)(t-c_1)^2\right]$, b_1, b_2, b_3, c_1, c_2 and c_3 are fixed parameters, and Φ^{-1} is the inverse standard normal cumulative distribution function. Based on the above specification (i.e. Equations (2) and (3)), the shape of temperature-dependent HC_ps would vary with the temperature because of its variation with model parameters (see Appendix A for more details).

3. Results

3.1. Temperature-dependent chemical toxicity (TDCT) to freshwater organisms

Across all 13 chemicals studied, the dataset contained 68 sets of acute toxicity data obtained from multiple studies for the meta-analysis (Table S1), and temperature–toxicity relationships are

shown in Fig. S2. Fifty-two per cent of the cases followed inverted V-shaped Model-II, and 26% of cases followed the negative linear Model I (Fig. 1a; see Fig. S3 for metal and species compositions for each model). In the remaining cases, 13% indicated the V-shape relationship (i.e. chemical toxicity interestingly decreased first and then increased with temperature), while 6% showed the positive linear relationship (i.e. chemical toxicity increased with increasing temperature). Additionally, 3% of the cases demonstrated no effect of temperature on chemical toxicity (i.e. neutral effect).

To rectify the potential errors and variations caused by different experimental conditions in different studies, we also examined 37 sets of toxicity data from individual studies conducted at multiple temperatures. Similarly, 53% and 30% of cases conformed to Model II and Model I, respectively (Fig. 1b). For the remaining cases, the V-shape relationship, positive linear relationship and neutral ones covered 8%, 3% and 6%, respectively. The results were in good agreement with those obtained from multiple studies (Fig. 1a; Fisher's exact test: calculated $X^2 = 18.3$; $p > 0.05$), indicating most freshwater species predominantly follow Model II (52–53%) and Model I (26–30%).

3.2. Temperature-dependent SSDs

Among all datasets for construction of temperature-dependent SSDs, some outliers were identified and excluded from our meta-analysis (Table S2). The remaining data points are listed in Table S3. For most of the 7 studied chemicals, temperature-dependent SSDs were visually diverged (Fig. 2a–g), indicating different community sensitivities at different temperatures. This was supported by significantly different slope and intercept parameters of their SSDs fitted with a log-normal regression model (Table S4) and different HC_{10} estimates (Table 1). Most temperature-dependent datasets contained good taxonomic diversity and covered a good coverage of species (Fig. 2 and Table S3). In general, datasets were dominated by crustaceans, fish, molluscs and insects, supplemented with algae, amphibians, worms and other invertebrates. Of the three models, no single category provided the best fit for all datasets, but Burr Type III model fitted best for most datasets (i.e. 26 out of 44; Table S5). By looking at the temperature-dependent HC_{10} values, an order-of-magnitude of differences in HC_{10} values existed under various test temperatures for most chemicals such as chlorpyrifos, copper, malathion, mercury and pentachlorophenol. Significant differences IN temperature-dependent HC_{10}s were also detected ($p < 0.05$; Tables 1 and S5).

We also noted apparent temperature-dependent differences among fish-specific SSDs to pentachlorophenol and among insect-specific SSDs to chlorpyrifos (Fig. 2h and i). Differences in temperature-dependent sensitivities were revealed for both taxa, as reflected by significant difference in HC_{10} values for different temperatures (Table 1). Regarding taxon-specific sensitivity, insects shared a similar sensitivity as that of chlorpyrifos with a mixture of global species (overlapping 95% CIs of pairwise HC_{10} values at a particular temperature), while fishes were more sensitive to pentachlorophenol than to a mixture of global species at 20 and 22 °C, respectively (95% CIs of pairwise HC_{10} values were not overlapped).

3.3. Temperature-dependent HC_{10}s

On the basis of derived temperature-dependent HC_{10} values obtained from global SSDs, an inverted V-shape (i.e. Model II) between temperature and HC_{10} values occurred across all seven tested chemicals (Fig. 3a–g). The largest HC_{10} value was at or around T_{opt} for each chemical (Tables 1 and S6). Based on Gaussian model, freshwater species had the lowest sensitivity to phenol, carbaryl, chlorpyrifos, copper, pentachlorophenol, mercury and malathion at 17.6, 17.9, 20.3, 20.5, 21.5, 22.0 and 23.5 °C, respectively. Interestingly, almost identical T_{opt} values were found for fish-specific SSDs and global SSDs to pentachlorophenol (21.7 °C and 21.5 °C, respectively). On the contrary, because of data limitation at low temperatures, the relationship between temperature and insect-specific HC_{10}s was linear from 20 °C to 25 °C (i.e. Model I; Fig. 3i).

3.4. Mathematical model for deriving temperature-dependent HC_p

Under the hypothesis of a temperature-dependent SSD model, the HC_ps were determined by two factors: temperature and model parameters. Mathematically, as expected from Equations (11) and (13) in Appendix A, $\partial^2 x/\partial t^2 < 0$ when $t <$ (or $>$) T_{opt} and $\partial^2 x/\partial t^2 > 0$ when $t = T_{opt}$, an inverted V-shaped TDCT pattern existed between temperature and the HC_ps.

By considering HC_{10} (i.e. given $p = 10$), the temperature-dependent HC_{10} values and T_{opt} were calculated using fixed model parameters (bs and cs) and model parameters (μ and σ), according to Equations (2) and (3), respectively (Tables 1 and S7). On the basis of predicted HC_{10} values, inverted V-shaped patterns were observed for 7 of the 9 examined SSDs, including carbaryl, chlorpyrifos, copper, malathion, pentachlorophenol, phenol and fish-specific to pentachlorophenol (Fig. S4). Similarly, a negative linear relationship existed for temperature effects to insect-specific HC_{10}s to chlorpyrifos. However, when compared to the results obtained from the meta-analysis for mercury (i.e. the inverted V-

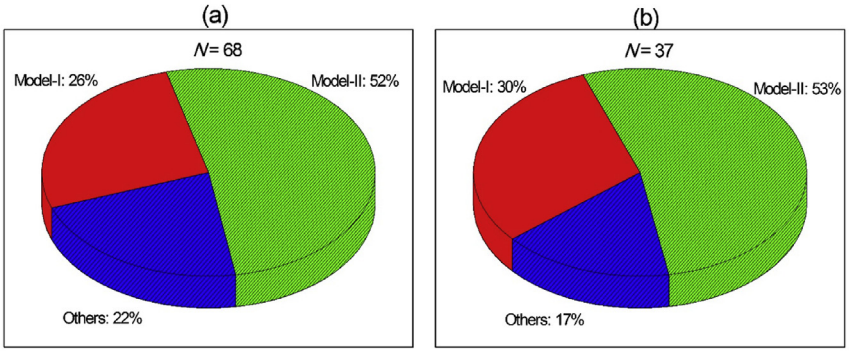

Fig. 1. Partitioning of different temperature-dependent chemical toxicity (TDCT) models for describing the acute sensitivity of various freshwater organisms exposed to each of thirteen chemicals along a temperature gradient. The meta-analysis was based on acute toxicity endpoints such as median lethal or effective concentration (LC_{50}/EC_{50}), and obtained from (a) multiple studies and (b) individual studies. *N* indicates total number of cases.

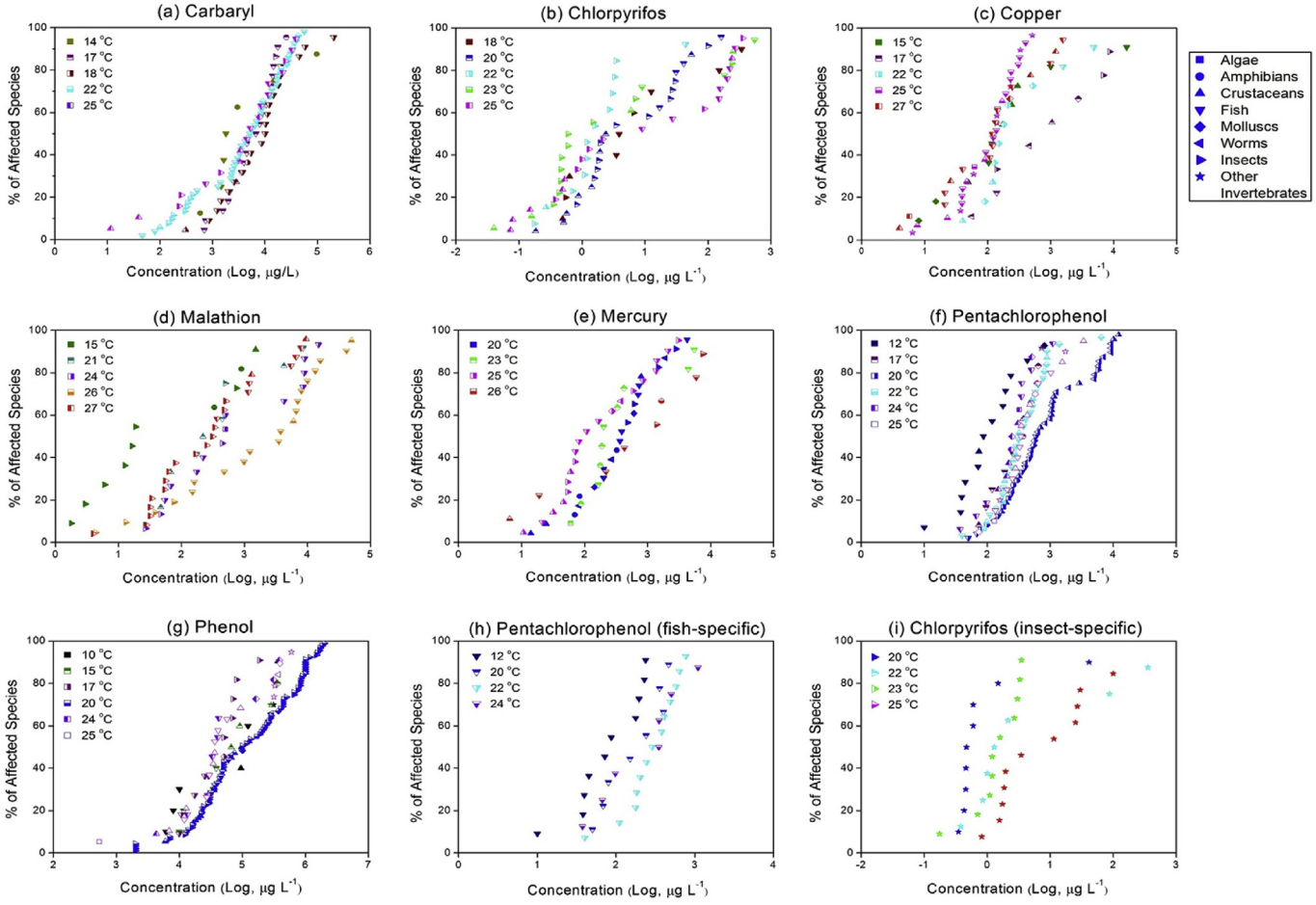

Fig. 2. Temperature-dependent species sensitivity distributions (SSDs) for (a) carbaryl; (b) chlorpyrifos; (c) copper; (d) malathion; (e) mercury; (f) pentachlorophenol; (g) phenol; (h) pentachlorophenol (fish-specific) and chlorpyrifos (insect-specific). Symbols for taxonomic groups are given in the legend at the right-top corner, and temperatures are indicated in different colours at the left-up corner of each graph (colour code: 10 °C in black. 12 °C in navy, 14 °C in dark yellow, 15 °C in olive, 17 °C in purple, 18 °C in wine, 20 °C in blue, 21 °C in dark cyan, 22 °C in cyan, 23 °C in green, 24 °C in violet, 25 °C in magenta, 26 °C in orange, and 27 °C in red). Multiple temperature-dependent SSDs for a chemical (global/taxon-specific) were presented using full-, (down, left, up, right) half-, and/or empty-filled symbols. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

shape; Fig. 3e), a negative linear relationship between temperature and HC_{10}s was obtained (Fig. S4e).

4. Discussion

4.1. Temperature-dependent chemical toxicity (TDCT) to freshwater organisms

As demonstrated in previous studies (e.g. Cairns et al., 1978; Lau et al., 2014; Zhou et al., 2014; Mu et al., 2018), the toxicity of chemicals on aquatic organisms can be greatly affected by temperature in a variety of ways. The results of the present meta-analysis demonstrated that the relationship between temperature and chemical toxicity for freshwater organisms can be jointly described by both Model I (26–30% of all cases) and Model II (52–53% of all cases). Rather than comparing toxicity differences among temperatures to a species from individual studies, our meta-analysis approach reveals the combined impact of the chemical exposure and temperature to the biological community (temperature-dependent SSDs). Our probabilistic approaches appear more reliable (robust) because these TDCT relationships are inherently data driven and account for inter-species variabilities than a particular toxicity testing conducted under strictly controlled laboratory conditions.

The observed TDCT responses in freshwater organisms can be explained by temperature-mediated changes (Fig. S5) in physical properties of the water environment (e.g. reduced gaseous dissolution at increased temperature), in characteristics of the chemical of concern (e.g. speciation, complexation and bioavailability) and biological responses (e.g. aerobic scope, chemical uptake and excretion). All these key processes are concomitantly governed by temperature, while the interaction among these processes consequently determines the chemical toxicity to the organisms.

Temperature can affect various physical parameters in water bodies, as well as chemical properties under different thermal dynamics. For example, a reduced gas solubility (e.g. oxygen) in water and inside aquatic organisms under high temperatures would reduce the aerobic scope of the organisms and cause physiological and biological damages (Pörtner, 2002). Temperature can also influence partition coefficient or diffusion rates of chemicals (Heugens et al., 2001), leading to aggregation and precipitation and, in turn, affecting their speciation, solubility and bioavailability (Bourgeault et al., 2013). Moreover, changes in water viscosity at lower temperatures can influence the swimming performance and kinematics of ectotherms (Fuiman and Batty, 1997) and then reduce their food ingestion (Bolton and Havenhand, 1998) and food

Table 1
The hazardous concentrations 10% (HC_{10}s; μg L^{-1}) and optimum temperature (T_{opt}) derived from temperature-dependent species sensitivity distributions (SSDs) and mathematical models, respectively. Superscript letters indicate significant different HC_{10} values among different temperature-dependent SSDs using parametric one-way analysis of variance (ANOVA) and Turkey's post hoc test (for carbaryl, chlorpyrifos, copper, malathion and phenol) or non-parametric Kruskal-Wallis test and Dunn's post-hoc test (for mercury, pentachlorophenol (all and fish-specific) and malathion (insects-specific); significance level $\alpha = 0.05$). $N_{sp.}$ and N_{taxa} indicate the total number of species and taxa, respectively, for an SSD. NA indicates that data are not available.

Chemical	Temperature (°C)	Temperature-dependent SSDs				Mathematical model	
		$N_{sp.}$	N_{taxa}	HC_{10} (95% CI)	T_{opt} (°C)	HC_{10}	T_{opt}
Carbaryl	14	7	3	170 (31, 463) [a]	17.9	226	18.6
	17	21	4	797 (672, 1047) [b]		731	
	18	21	3	774 (659, 927) [b]		839	
	22	50	5	190 (158, 236) [a]		408	
	25	18	5	114 (80, 197) [a]		62.7	
Chlorpyrifos	18	9	3	0.12 (0.03, 0.30) [ac]	20.3	0.171	20.4
	20	21	3	0.49 (0.32, 0.63) [b]		0.167	
	22	12	3	0.22 (0.13, 0.35) [a]		0.123	
	23	16	3	0.12 (0.06, 0.17) [ac]		0.095	
	25	15	3	0.07 (0.03, 0.14) [c]		0.045	
Copper	15	10	3	11 (8.0, 43) [abd]	20.5	7.43	22.1
	17	8	5	34 (17, 54) [bc]		18.5	
	22	10	3	59 (41, 78) [c]		36.3	
	25	27	4	20 (17, 23) [d]		18.1	
	27	17	4	7.6 (5.6, 9.9) [a]		7.21	
Malathion	15	10	3	1.7 (1.4, 2.7) [a]	23.5	0.76	23.4
	21	10	3	25 (13, 33) [b]		14.9	
	24	14	3	36 (18, 60) [b]		21.9	
	26	18	3	27 (20, 46) [b]		18.8	
	27	19	3	13 (10, 18) [d]		15.4	
Mercury	20	22	6	54 (38, 57) [a]	22	40.6	21.2
	23	10	4	78 (51, 99) [b]		28.6	
	25	18	6	25 (17, 28) [c]		12.7	
	26	8	4	6.4 (1.7, 13) [d]		7.08	
Pentachlorophenol	12	12	3	17 (14, 21) [a]	21.5	12.3	22.7
	17	11	5	58 (49, 75) [b]		65.3	
	20	33	7	126 (119, 135) [c]		96.9	
	22	28	5	99 (85, 110) [d]		97.8	
	24	15	5	83 (61, 110) [bd]		80.7	
	25	19	5	96 (83, 111) [d]		67.9	
Phenol	10	9	5	3980 (1110, 7740) [a]	17.6	3790	17.7
	15	9	5	7430 (4310, 11000) [ab]		8330	
	17	10	3	8670 (6250, 11100) [b]		9120	
	20	87	6	8210 (4900, 10600) [b]		8190	
	24	10	3	4910 (2800, 7150) [a]		4520	
	25	15	6	3360 (1840, 5050) [a]		3600	
Pentachlorophenol (fish-specific)	12	10	–	12 (7.0, 19) [a]	21.7	14.5	19.8
	20	8	–	34 (19, 60) [b]		41.1	
	22	13	–	78 (64, 96) [c]		40.6	
	24	7	–	17 (6.0, 44) [ab]		36.0	
Chlorpyrifos (insects-specific)	20	11	–	0.61 (0.29, 1.30) [a]	NA	0.581	15
	22	10	–	0.36 (0.23, 0.57) [b]		0.146	
	23	9	–	0.35 (0.07, 1.78) [b]		0.083	
	25	7	–	0.14 (0.01, 1.3) [b]		0.034	

conversion ratio (Abbink et al., 2012).

The temperature–toxicity relationship was partly thought to be related to changes in accumulation kinetics (Heugens et al., 2003). Chemical toxicity is not only associated with the concentration in the water but also linked to speciation, solubility and bioavailability (Bourgeault et al., 2013). Chemical bioavailability is controlled by thermodynamics (i.e. speciation), and bonding interaction kinetics between ions or their complex species of the ions and the cell membrane or cell wall (Benda and Kouba, 1991). Higher temperature increases the rate of uptake and bioaccumulation of chemical contaminants because of increased metabolic rate and ventilation rate of ectotherms at elevated temperatures (Cairns et al., 1978; Graney et al., 1984). On the other hand, the temperature dependence of chemical elimination appears to be less clear in aquatic organisms. For instance, a small but significant temperature effect on elimination was found in isopods because the metal was eliminated at 5 °C but not at 10 °C and 20 °C (van Hattum et al., 1993).

Most freshwater creatures are ectothermic, and their metabolisms are highly temperature dependent (Cherkasov et al., 2006), also making temperature a key environmental factor in controlling their physiological performances, such as feeding rate and resource acquisition (van der Have, 2002), ventilation and blood circulation (Vellinger et al., 2012) and thus fitness (e.g. development, growth, survivorship and reproduction) (Kingsolver, 2009; Amarasekare and Savage, 2012). The oxygen-limited thermal tolerance model also suggests that aquatic ectotherms, like fish, generally live within a confined range of temperatures (i.e. a range of tolerable temperatures) where they function aerobically without displaying any sign of stress (Frederich and Pörtner, 2000). However, beyond this thermal tolerance window, the ectotherms encounter a mismatch of energy demand and supply, experience restricted oxygen availability and, eventually, shift to anaerobic respiration at the extreme high or low temperatures to increase energy supply for sustaining essential cellular and physiological functions (Pörtner

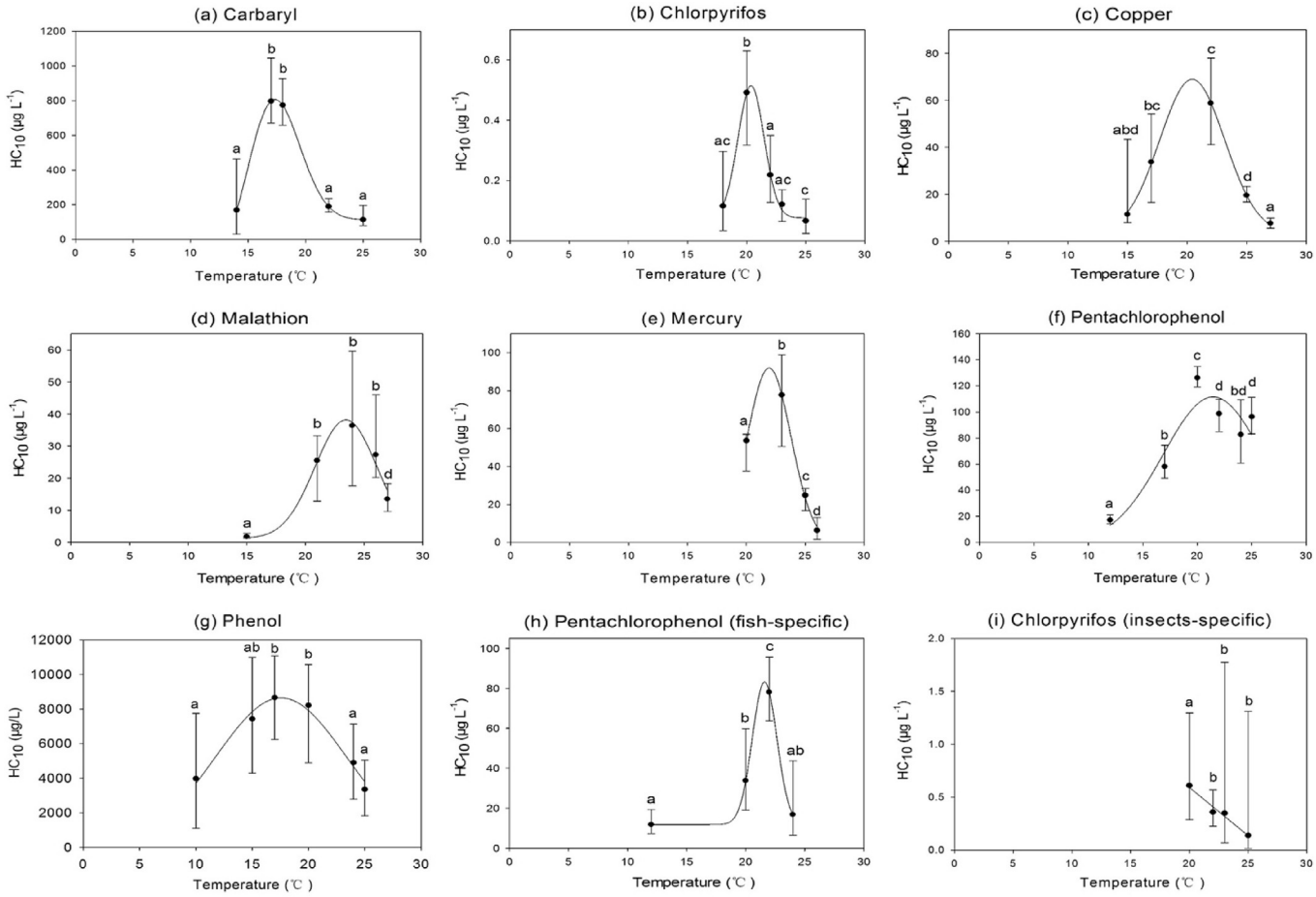

Fig. 3. Relationships between temperature and hazardous concentrations 10% (HC_{10}s) for (a) carbaryl; (b) chlorpyrifos; (c) copper; (d) malathion; (e) mercury; (f) pentachlorophenol; (g) phenol; (h) pentachlorophenol (fish-specific) and (i) chlorpyrifos (insects-specific). Error bars indicate 95% confidence interval of each HC_{10}. Different letters indicate significant differences of temperature-dependent HC_{10} values for each chemical (significance level $\alpha = 0.05$).

and Knust, 2007). Evidence showed that oxygen deficiency (e.g. hypoxia) could elicit (1) the transition to passive tolerance and associated systemic and cellular stress signals such as hormonal responses or oxidative stress (Bly and Clem, 1992; Chang et al., 2009; Vinagre et al., 2014); and (2) the activation of protection mechanisms (e.g. induction of cold or heat shock proteins) at thermal extremes (Pörtner and Knust, 2007). As exposure to either cold or heat extremes can be crucial to aquatic ectotherms (e.g. acclimation and adaption) (Bokhorst et al., 2008), they have to adjust their physiological and biochemical responses to overcome such a stressful thermal scenario.

As shown in this study, additional temperature–toxicity relationships were also found, suggesting that the TDCT patterns considerably varied among species, among chemicals and between different tests. For cases with a positive linear relationship, the evaporation rate of chemicals with low vapour pressures (e.g. pentachlorophenol and phenol) increases with temperature and hence reduces the chemical concentration, uptake and bioaccumulation and lowers toxicity (Magallona, 1994). Alternatively, freshwater species such as the burrowing mayfly nymph (*Hexagenia rigida*) can be effective in eliminating cadmium at high temperatures, leading to a low toxicity (Odin et al., 1997).

For cases with a V-shape relationship, protective or anaerobic enzymes can be induced at low and high temperatures as a means of cellular protection or restoration of damaged structures. This biochemical protection and detoxification mechanisms may increase with increasing and decreasing temperature from the T_{opt}, which then can reduce toxicity at temperatures higher or lower than T_{opt} (Howe et al., 1994). In fact, stress proteins such as heat/cold shock proteins can be induced to protect cellular structures (e.g. DNA) and repair damaged components, and in this way, the aquatic ectotherm could extend its survivability even though in a time-limited manner at the thermal extremes (Pörtner, 2002). These differing, and sometimes contradictory, theories invite further studies and laboratory validations with a wide range of chemicals and aquatic organisms.

4.2. Temperature-dependent SSDs and HC_{10} values

Because the interactions between temperature and chemical contaminants are complicated, a source of uncertainty (e.g. temperature-mediated chemical toxicities; Fig. S5) will be introduced if effects of temperature are ignored with regard to the SSD modelling for establishing WQGs or conducting ecological risk assessment. This study, for the first time, has examined temperature-dependent SSDs for freshwater organisms. The crucial insight emerging from the current meta-analysis is the effect of temperature on HC_{10} values derived from the temperature-dependent SSDs, which follow a general inverted V-shaped relationship along a temperature gradient (i.e. Model II). We have also shown that the temperature component of SSD modelling cannot be ignored because critical quantities, such as the HC_p, are highly

temperature dependent. This model will be useful to refine WQGs at various naturally relevant temperatures.

Sources of uncertainty included synergistic effects of other potentially confounding abiotic factors (e.g. pH and hardness), genetic and geographical differences of species sensitivities, species composition of the SSD, inherent biological differences among different species (Kwok et al., 2007), as well as data quality and quantity (Wheeler et al., 2002; Dowse et al., 2013). Additionally, the model selection for fitting an SSD and determining the HC_{10} (or other HC_p) could also be a source of uncertainty (Wheeler et al., 2002; Wang et al., 2014). For instance, a different temperature–HC_{10} relationship (negative linear Model I; Fig. S4e) was obtained by the mathematical model for mercury when compared with that revealed in the meta-analysis (inverted V-shaped Model II; Fig. 3e). This may be due to the highly model-dependent HC_{10} values between log-normal and Burr Type III regression models. When we re-estimated the HC_{10}s for mercury temperature-dependent SSDs by using log-normal model only, HC_{10}s for 20 °C, 23 °C, 25 °C and 26 °C were 41 (34, 48) μg L^{-1}, 26 (8, 55) μg L^{-1}, 15 (11, 19) μg L^{-1} and 6.5 (1.7, 13) μg L^{-1}, respectively, which apparently followed a negative linear relationship between temperature and HC_{10}s (i.e. Model I). Further study should be warranted when there are more toxicity data available, especially for high-quality data, to investigate the effects of abiotic factors (e.g. temperature, pH and hardness) on chemical toxicity to freshwater species. Alternatively, further studies can also explore the application of quantitative structure–activity relationship model to normalise the test conditions other than temperature. Overall, this study provides a scientific and practical framework to better control and manage chemical contaminants under different temperature regimes.

5. Conclusion

At present, most environmental authorities derive WQGs of chemicals based on acute or chronic toxicity data that are generated from a fixed temperature (US EPA, 1998; ASTM International, 2003). It is questionable whether or not these WQGs offer adequate protection of aquatic biota exposed to a wide range of temperatures that fluctuate daily, seasonally and annually. Our results suggest that in most cases, freshwater species exhibit the highest tolerance towards chemicals at their physical optimal temperature (T_{opt}) where the chemical toxicity is lowest, and chemical toxicity exacerbates when temperature is higher or lower than T_{opt} (i.e. inverted V-shaped relationship). The present study also clearly indicates that both SSDs and HC_{10} are temperature dependent and generally follow the inverted V-shaped trend. With the mathematical model developed in this study, it is now possible to predict HC_{10} (or other HC_p) at relevant ambient temperatures, provided there are enough data for constructing temperature-dependent SSDs. Such inclusion of temperature as a covariate can further enhance the ecological realism and accuracy of the derivation of site-specific WQGs, particularly in the face of global climatic change.

Conflicts of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.02.103.

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